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<b>(54) Title:</b> WET PROCESSING METHODS FOR THE MANUFACTURE OF ELECTRONIC COMPONENTS USING OZONATED PROCESS FLUIDS  <b>(57) Abstract</b>  The present invention is directed to methods of wet processing electronic components using ozonated process fluids. In the methods of the present invention, the electronic components are contacted with a wetting solution, and contacted with an ozonated process fluid containing gaseous ozone. The contacting of the electronic components with an ozonated process fluid is performed in the presence of a base. The methods of the present invention are particularly useful for removing organic materials from surfaces of electronic components.		

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## **WET PROCESSING METHODS FOR THE MANUFACTURE OF ELECTRONIC COMPONENTS USING OZONATED PROCESS FLUIDS**

### **CROSS-REFERENCE TO RELATED APPLICATIONS**

This application claims the benefit of U.S. Provisional Application Ser. No.  
5 60/094,545, filed on July 29, 1998, the disclosure of which is hereby incorporated by  
reference in its entirety.

### **FIELD OF THE INVENTION**

The present invention is directed to wet processing methods for the  
manufacture of electronic components including electronic component precursors. More  
10 specifically, this invention relates to methods of processing electronic components using  
ozonated process fluids.

### **BACKGROUND OF THE INVENTION**

Wet processing of electronic components, such as semiconductor wafers, flat panels,  
and other electronic component precursors is used extensively during the manufacture of  
15 integrated circuits. Semiconductor fabrication is described generally, for example, in P. Gise  
*et al.*, Semiconductor and Integrated Circuit Fabrication Techniques (Reston Publishing Co.  
Reston, Va. 1979), the disclosures of which are herein incorporated by reference in their  
entirety.

Preferably, wet processing is carried out to prepare the electronic components for  
20 processing steps such as diffusion, ion implantation, epitaxial growth, chemical vapor  
deposition, and hemispherical silicon grain growth, or combinations thereof. During wet  
processing, the electronic components are contacted with a series of processing solutions. The  
processing solutions may be used, for example, to etch, to remove photoresist, to clean, to

grow an oxide layer, or to rinse the electronic components. *See, e.g.*, U.S. Patent Nos. 4,577,650; 4,740,249; 4,738,272; 4,856,544; 4,633,893; 4,778,532; 4,917,123; and EP 0 233 184, assigned to a common assignee, and Burkman *et al.*, *Wet Chemical Processes-Aqueous Cleaning Processes*, pg 111-151 in Handbook of Semiconductor Wafer Cleaning Technology  
5 (edited by Werner Kern, Published by Noyes Publication Parkridge, New Jersey 1993), the disclosures of which are herein incorporated by reference in their entirety.

There are various types of systems available for wet processing. For example, the electronic components may be processed in a single vessel system closed to the environment (such as a Full-Flow™ system supplied by CFM Technologies, Inc.), a single vessel system  
10 open to the environment, or a multiple open bath system (e.g., wet bench) having a plurality of baths open to the atmosphere.

Following processing, the electronic components are typically dried. Drying of the semiconductor substrates can be done using various methods, with the goal being to ensure that there is no contamination created during the drying process. Methods of drying include  
15 evaporation, centrifugal force in a spin-rinser-dryer, steam or chemical drying of wafers, including the methods and apparatus disclosed in, for example, U.S. Pat. Nos. 4,778,532 and 4,911,761.

An important consideration for an effective wet processing method is that the electronic component produced by the process be ultraclean (*i.e.*, with minimum particle  
20 contamination and minimum chemical residue). An ultraclean electronic component is preferably free of particles, metallic contaminants, organic contaminants, and native oxides; has a smooth surface; and has a hydrogen-terminated surface. Although wet processing methods have been developed to provide relatively clean electronic components, there is always a need for improvement because of the intricacies associated with technological  
25 advances in the semiconductor industry. One of the most challenging problems of attaining ultraclean products is the removal of photoresist.

The use of ozone for removing organic material, such as photoresist, from semiconductor wafers has been investigated. For example, U.S. Patent No. 5,464,480 issued to Matthews (hereinafter "Matthews"), describes a process in which semiconductor wafers are  
30 contacted with a solution of ozone and water at a temperature of about 1°C to about 15°C. Matthews discloses, for example, placing the semiconductor wafers into a tank containing deionized water, diffusing ozone into the deionized water for a time sufficient to oxidize the

organic materials from the wafers, while maintaining the temperature of the water at between about 1°C to about 15°C, and then rinsing the wafers with deionized water. Matthews further discloses exposing the wafers to ultraviolet light during the process.

Various other methods have been investigated using ozone in conjunction with water to strip organic materials from the surface of semiconductor wafers or to rinse wafers after chemical processing. For example, in one such method, ozone gas is generated in an ozone generator and fed to an ozonator where the ozone gas is mixed with DI water. The ozone gas is also simultaneously fed to the bottom of the process vessel via specially designed device that provides a uniform stream of gaseous ozone into the bath. *Matthews et al., Mat. Res. Soc. Symp. Proc.*, **1997**, 477, 173-78. See also 1997 Joint Int's Mtg. of Electro. Chem. Soc'y and Int'l Soc'y. of Electro., Abstract 1886, p. 2169 submitted by Kenens et al.; *Id.* at Abstract 1887, p. 2170, submitted by Wolke et al.; *Id.* at Abstract 1892, p. 2176, submitted by Fukazawa et al.; *Id.* at Abstract 1934, p. 2236, submitted by Kashkoush et al.; *Id.* at Abstract 1890, p. 2173, submitted by Li et al.; *Id.* at Abstract 1891, p. 2174, submitted by Joo et al.; Ultra Clean Processing of Silicon Surfaces UCPSS '96, Kenens et al., *Removal of Organic Contamination From Silicon Surfaces*, p. 107-110.

In another method, the use of ozone-injected ultrapure water (ozone concentration of about 1-2 ppm) is applied to the RCA cleaning method. The ozonated water is used to remove organic impurities. The wafers are then treated with  $\text{NH}_4\text{OH}$  and  $\text{H}_2\text{O}_2$  to remove organic and metal particles, followed by a treatment with  $\text{HF}$  and  $\text{H}_2\text{O}_2$  to remove native oxide, metal, and to improve surface smoothness. The wafers are then rinsed with DI water. The ozone gas is generated by electrolyzing ultra pure water. The generated ozone gas is then dissolved in ultrapure water through a membrane. Ohmi et al., *J. Electrochem. Soc'y*, **140**, **1993**, 804-10.

Another method uses a moist ozone gas phase. In this method, a quartz container is filled with a small amount of liquid, sufficient to immerse the  $\text{O}_3$  diffuser. The liquid is DI water spiked with additives such as hydrogen peroxide or acetic acid, if appropriate. A lid is placed on the container and the liquid is heated to 80°C. Wafers are placed directly above the liquid interface, they are not immersed in the liquid. Heating of the liquid in a sealed container and continuous  $\text{O}_3$  bubbling through the liquid exposes the wafers to a moist ambient  $\text{O}_3$  environment. *De Gendt et al., Symp. VLSI Tech. Dig. Tech. Papers*, **1998**, 168-69. The *De Gendt* paper further describes a method whereby a quartz tank is filled with 7 liters of liquid, an ozone diffuser is located at the bottom of the tank, and the liquid can be heated.



The wafers are positioned directly above the ozone diffuser and immersed in the liquid such that  $O_2/O_3$  bubbles contact the wafer surfaces. The *De Gendt* paper also reports that OH radical scavengers such as acetic acid can enhance process efficiency.

In another method, photoresist removal is carried out in a gas phase reactor at a temperature of between about 200-300°C. In certain instances, additives such as  $N_2O$  gas are mixed with the ozone gas. See Olness *et al.*, Mat. Res. Soc'y. Symp., 135, 1993, 261-66.

Spin cleaning techniques using ozonated water have also been investigated. See, e.g., Cleaning Technology In Semiconductor Device Manufacturing Symposium, Yonekawa *et al.*, Contamination Removal By Wafer Spin Cleaning Process With Advanced Chemical Distribution System, 94-7, 94-101; 1997 Joint Int's Mtg. of Electro. Chem. Soc'y and Int'l Soc'y. of Elctro., Abstract 1888, p. 2171 submitted by Osaka *et al.*

The use of ozone with cleaning solutions has also been investigated. One such method uses a wafer cleaning sequence with a single-wafer spin using ozonated water and dilute HF to remove contaminants such as particles, metallics, and organics from the wafer surfaces. The method consists of pouring ozonated water on a wafer surface for 10 seconds, followed by pouring dilute HF over the wafers for 15 seconds. This cycle is repeated until the desired results are achieved. 1997 Joint Int's Mtg. of Electro. Chem. Soc'y and Int'l Soc'y. of Elctro., Abstract 1888, p. 2171 submitted by Tsutomu *et al.*; see also *Id.* at Abstract 1889, p. 2172, submitted by Han *et al.*; *Id.* at Abstract 1892, p. 2176, submitted by Fukazawa *et al.*; Ultra Clean Processing of Silicon Surfaces UCPSS '96, Kennens *et al.*, Removal of Organic Contamination From Silicon Surfaces, p. 107-10.

Cleaning of semiconductor wafers has also been carried out using gaseous ozone and other chemicals such as hydrofluoric acid and hydrochloric acid to remove residual contaminating particles. For example, U.S. Patent No. 5,181,985 to Lampert *et al.*, ("Lampert") discloses a cleaning process where a water is sprayed at a temperature of 10 °C to 90 °C onto semiconductor wafers and a chemically active gaseous substance such as ammonia, hydrogen chloride, ozone, ozonized oxygen, chlorine, or bromine is introduced. In Lampert, ozone or ozonized oxygen is used to form a superficial oxide which is then subsequently removed with hydrofluoric acid or hydrochloric acid.

Ozone has also been used in conjunction with sulfuric acid as a means for stripping photoresist from semiconductor wafers. See, e.g., U.S. Patent Nos. 4,899,767 and 4,917,123

issued to CFM Technologies. The methods described in the CFM patents are carried out in a single vessel system and, generally, a solution of sulfuric acid is spiked with an oxidizing agent such as ozone. Other systems using sulfuric acid in conjunction with ozone may employ a gas distribution system that includes a sparger plate with holes for distributing gas through a bath in the tank. *See, e.g.*, U.S. Patent No. 5,082,518 assigned to SubMicron. SubMicron's patent describes the use of an apparatus that distributes ozone directly into the treatment tank containing the sulfuric acid.

Ozone ashing has also been investigated as a means for removing photoresist material from wafers. In this method, photoresist is oxidized at higher temperatures (250-350°C) by two strong oxidizing gases, ozone and atomic oxygen. A small amount of excited nitrous oxide enhances the ashing rate. *See Olness et al.*, Mat. Res. Soc'y. Symp., 135, 1993, 261-66.

U.S. Patent No. 5,503,708 to Koizumi *et al.*, ("Koizumi") discloses an alternative apparatus and method using gaseous ozone for removing a photoresist film from a semiconductor wafer. In Koizumi, an apparatus is used that processes a single wafer at a time. The apparatus exposes the wafer to a gas mixture containing ozone and alcohol while the wafer surface is preferably heated to a temperature of 150 °C to 250 °C to effect removal of the photoresist.

The use of ozone in precleaning steps has also been explored. In one such method, such as disclosed in U.S. Patent No. 5,762,755 to McNeilly *et al.*, a wafer contaminated with organics is held in a partial vacuum and heated to at least 200°C by radiation and then exposed to ozone. The wafer is then cooled to at or below 80°C and then exposed to ultraviolet excited chlorine.

Another method for pre-cleaning wafers uses an O<sub>3</sub>/IR process as an *in situ* cleaning step for organic removal before oxide etching to condition the surface and to assure etch repeatability and uniformity. As a post-treatment step, a thin layer of oxide may be grown on the wafer surface. In this process, the ozone is fed into the process chamber while the wafer is being heated by an infra red lamp to a certain temperature, after which the ozone is turned off and the wafer is cooled down by a low temperature inert gas. Cleaning Technology In Semiconductor Device Manufacturing Symposium, Kao *et al.*, *Vapor-Phase pre-Cleans for Furnace-Grown and Rapid-Thermal Thin Oxides*, 1992, 251-59.

The use of ozone gas in conjunction with ultraviolet light for cleaning and etching wafer surfaces has also been investigated. *See Semiconductor Wafer Cleaning and Surface*

Characterization (proceedings of the 2<sup>nd</sup> workshop), Moon, *Si Wafer Cleaning Study by UV/Ozone and In Situ Surface Analysis*, 68-76; ASM Int'l, Li *et al.*, *UV/Ozone Pre-Treatment on Organic Contaminated Wafer for Complete Oxide Removal in HF Vapor Cleaning*.

5           Although the use of ozone has been investigated for use in wet processing techniques, there are still many drawbacks. For example, one problem associated with the use of ozone when dissolved in water is that the mass transfer rate of ozone to an electronic component is quite slow. Additionally, when ozone is dissolved in water, the ozone decays very fast. This decay of ozone can be even further accelerated by such factors as increasing the pH of the  
10       solution. Thus, there is a need to provide ozone in a stable form that is readily deliverable to the surfaces of the electronic components.

Although gaseous ozone has been used alone and in combination with other gaseous substances to improve the rate of processing of electronic components, the use of gaseous ozone has disadvantages as well. For example, gaseous ozone undesirably leaves oxidized organic by products on the electronic components which must subsequently be removed, often requiring additional apparatuses. Furthermore, processing, especially when performed to remove photoresist, is typically done at high temperatures (greater than 150 °C and more commonly greater than 250 °C). These high temperatures can lead to malfunctions in the electronic component. Another disadvantage is that many systems currently used for processing electronic components with gaseous ozone process a single wafer at one time and/or are not able to perform several processing steps in one vessel.

Thus, there is the need in the art for a simple and efficient method that permits the safe chemical treatment of electronic components with ozone, while at the same time providing an environmentally safe and economical method.

25           The present invention meets these as well as other needs. For example, the present invention provides methods of readily delivering ozone in a stable form to electronic components during wet processing. Also for example, the present invention provides methods for exposing the electronic components to gaseous ozone and other processing solutions in a series of steps in a single vessel.

30 SUMMARY OF THE INVENTION

The present invention provides, *inter alia*, wet processing methods for the manufacture of electronic components, including electronic component precursors such as semiconductor



wafers used in integrated circuits. More specifically, this invention relates to methods of, for example, processing electronic components using wet processing techniques with ozonated process fluids. In particular, the methods of the invention may be used, *inter alia*, to remove organic materials, such as photoresists, from electronic components and to oxidize the surfaces of the electronic components (i.e., growth of an oxide layer). The methods of the present invention may also be used in pretreatment steps such as cleaning or etching.

In one embodiment of the present invention, a method is provided for wet processing electronic components including contacting the surfaces of the electronic components with a wetting solution to wet the surfaces of the electronic components with the wetting solution, where the wetting solution contains water; forming an ozonated process fluid containing gaseous ozone where the ozonated process fluid is in the form of a gas, vapor, mist, or mixtures thereof; and contacting the electronic components with the ozonated process fluid in a reaction chamber for a contact time and in the presence of at least one base for at least a portion of the contact time, where the ozonated process fluid is in the temperature range of about 20 °C to about 145 °C, and the base is present in the wetting solution or the ozonated process fluid, or combinations thereof.

In another embodiment of the present invention, a method is provided for wet processing electronic components that includes loading in an enclosable single vessel a plurality of electronic components; contacting the surfaces of the electronic components with a wetting solution to wet the surfaces of the electronic components with the wetting solution, where the wetting solution contains water; forming an ozonated process fluid containing gaseous ozone where the ozonated process fluid is in the form of a gas, vapor, mist, or mixtures thereof; contacting the electronic components with the ozonated process fluid in a reaction chamber for a contact time and in the presence of at least one base for at least a portion of the contact time, where the ozonated process fluid is in the temperature range of about 20 °C to about 145 °C, and the base is present in the wetting solution or the ozonated process fluid, or combinations thereof; and contacting the electronic components in the vessel with one or more processing solutions after the contacting of the electronic components with the ozonated process fluid.

In yet another embodiment of the present invention, a method is provided for wet processing electronic components that includes contacting electronic components with a wetting solution to wet the surfaces of the electronic components with the wetting solution,

where the wetting solution contains water and at least one base; contacting the wetted electronic components with an ozonated process fluid for a contact time, where the ozonated process fluid is in the form of a gas, vapor, mist, or mixtures thereof, and where the ozonated process fluid is in the temperature range of about 20 °C to about 145 °C; and contacting the  
5 electronic component with one or more processing fluids after the contacting of the electronic components with the gaseous ozone.

### DETAILED DESCRIPTION OF THE INVENTION

The present invention provides methods of wet processing electronic components using an ozonated process fluid. The methods of the present invention are particularly useful for  
10 removing organic materials from the surfaces of electronic components using the ozonated process fluid. For example, during wet processing, the methods of the present invention can remove organic materials such as photoresists (ashed or unashed), plasticizers, surfactants, fluorocarbon polymers, organics from human contact or combinations thereof. The methods of the invention may also be used to grow an oxide layer on the electronic component surface.  
15 The methods of the invention are also contemplated to be used for pre-treatment cleaning, cleaning in between processing steps, and post-treatment cleaning and processing (e.g., oxide growth).

The present invention also provides methods of using an ozonated process fluid where a plurality of electronic components can be treated with the ozonated process fluid  
20 simultaneously and/or where the electronic components can be subsequently contacted with other process fluids in the same vessel.

The terminology "wet processing" or "wet process" as used herein means the electronic components are contacted with one or more liquids (hereinafter referred to as "process liquids" or "process solutions") to process the electronic components in a desired manner. For  
25 example, it may be desired to treat the electronic components to clean, etch, or remove photoresist from the surfaces of the electronic components. It may also be desired to rinse the electronic components between such treatment steps.

Wet processing may also include steps where the electronic components are contacted with other fluids, such as a gas, a vapor, or a liquid mixed with a vapor or gas, or combinations  
30 thereof. As used herein, the term "process fluid" includes liquids, gases, liquids in their vapor phases, or combinations thereof. The terminology "vapor" as used herein is meant to include partially vaporized liquid, saturated vapor, unsaturated vapor, supersaturated vapor or

combinations thereof. The terminology "mist" as used herein means a spray of liquid droplets. For example, the mist may be a spray of droplets preferably ranging in size from about 10  $\mu\text{m}$  to about 1500  $\mu\text{m}$ , more preferably from about 50  $\mu\text{m}$  or lower and most preferably from about 30  $\mu\text{m}$  or lower.

5           There are various types of process fluids used during wet processing. Generally, the most common types of process fluids used during wet processing are reactive chemical process fluids or liquids, and rinsing fluids or liquids. The terminology "reactive chemical process fluid" or "reactive chemical process liquid" as used herein, is any liquid or fluid that reacts in some desired manner with the surfaces of the electronic components to alter the surface  
10 composition of the electronic component. For example, the reactive chemical process liquid or fluid may have activity in removing contamination adhered or chemically bound to the surfaces of the electronic components, such as particulate, metallic, photoresist, or organic materials; activity in etching the surfaces of the electronic component; or activity in growing an oxide layer on the surface of the electronic component. As used herein, "rinsing liquid" or  
15 "rinsing fluid" refers to DI water or some other liquid or fluid that removes from the electronic components and/or vessel residual reactive chemical process fluids, reaction by-products, and/or particles or other contaminants freed or loosened by the chemical treatment step. The rinsing liquids or fluids may also be used to prevent redeposition of loosened particles or contaminants onto the electronic components or vessel. Examples of reactive chemical  
20 process fluids and rinsing fluids useful in the methods of the present invention are described in more detail hereinafter.

As used herein, "chemical treatment step" or "wet processing step" refers to contacting the electronic components with a reactive chemical process fluid or process fluid respectively.

25           The terminology "reaction chamber," as used herein, refers to vessels (enclosed or open to the atmosphere), baths, wet benches and other reservoirs suitable for wet processing electronic components. The terminology "single vessel," refers to any wet processing system in which the electronic components are maintained in one vessel during the entire wet processing sequence.

30           The terminology "electronic components," as used herein, includes for example electronic component precursors such as semiconductor wafers, flat panels, and other components used in the manufacture of electronic components (*i.e.*, integrated circuits); CD ROM disks; hard drive memory disks; or multichip modules.

In the methods of the present invention, the electronic components are contacted with a wetting solution and an ozonated process fluid, where at least one base is present for at least a portion of the contact time that the electronic components are contacted with the ozonated process fluid. The base may be present for example in the wetting solution, the ozonated  
5 process fluid, or both.

Although in no way intending to be bound by theory, it is believed that the base present in the wetting solution and/or ozonated process fluid enhances the reaction of ozone with the electronic components in the following manner. The presence of a base enhances the formation of hydroxide ions in the presence of compounds containing hydroxide functional  
10 groups (e.g., ammonia in the presence of water) or directly provides a source of hydroxide ions (e.g., ammonium hydroxide). It is believed that the hydroxide ions react with ozone to form hydroxyl radicals. These hydroxyl radicals are believed to be more effective in removing or oxidizing contaminants such as organic materials found on the surfaces of electronic components in comparison to ozone. Particularly, the hydroxyl radicals are believed to react  
15 quickly and nonselectively with the saturated and unsaturated carbon-carbon bonds typically found in organic materials to form such oxidation reaction products as CO, CO<sub>2</sub>, H<sub>2</sub>O, or combinations thereof. In comparison, although gaseous ozone will react with organic materials, the reaction with gaseous ozone is more selective and slower.

One difficulty in forming hydroxyl radicals is that the stability of ozone decreases with  
20 increasing pH so that the presence of the base may actually inhibit the formation of hydroxyl radicals. Additionally, even if hydroxyl radicals are formed, they have very short lives (e.g. seconds). Thus, the base and ozone are preferably added in a manner to facilitate the formation of hydroxyl radicals at or near the surfaces of the electronic components as described in more detail hereinafter.

25 The wetting solution may be any liquid that contains water that is capable of wetting the surfaces of the electronic components. By "wet" or "wetting" it is meant that the wetting solution when contacted with the electronic components preferably forms a layer of wetting solution that coats the electronic components. Although in no way intending to be bound in theory, it is believed that this layer provides an effective medium for the ozone to react to form  
30 hydroxy radicals at or near the surfaces of the electronic components, and/or to react directly with the surfaces of the electronic components. Preferably, the layer of wetting solution is continuous so that ozone can react uniformly on the surfaces of the electronic components.



Preferably, the thickness of the layer is relatively thin to ensure that the ozone forms hydroxyl radicals close enough to the surfaces of the electronic components for reaction (e.g., preferably about 40  $\mu\text{m}$  or less).

In addition to water, the wetting solution may also contain other compounds, that are preferably water soluble, to promote the formation of hydroxyl radicals. For example, the compound may contain hydroxyl functional groups that are capable of generating hydroxyl radicals in the presence of ozone or water. Examples of compounds that promote the formation of hydroxyl radicals include for example, hydrogen peroxide, bases, or combinations thereof. Bases that can be present in the wetting solution include for example inorganic bases or organic bases, such as ammonia, ammonium hydroxide, alkyl ammonium hydroxides, such as trimethyl ammonium hydroxide, alkali or alkaline earth metal hydroxides such as sodium hydroxide or potassium hydroxide, organic amines, basic amino acids, or combinations thereof. Preferred bases include ammonium hydroxide, alkyl ammonium hydroxides, alkali metal hydroxides, alkaline earth metal hydroxides or combinations thereof. The preferred amount of such compounds in the wetting solution will depend on the compound chosen. In the case of a base, preferably the base is added in an amount to provide a pH in the wetting solution of from about 9 to about 13. In the case of hydrogen peroxide, preferably hydrogen peroxide is present in the wetting solution at a concentration of from about 0.01 moles per liter to about 0.5 moles per liter, and more preferably from about 0.05 moles per liter to about 0.2 moles per liter.

The electronic components may be contacted with the wetting solution in any manner that wets the surfaces of the electronic components with the wetting solution. For example, the electronic components may be immersed and withdrawn from a wetting solution. The electronic components may also be placed in a vessel, where the vessel is filled and then drained of the wetting solution. The wetting solution may also be applied to the electronic components as a mist. Thus, there are various ways to contact the wetting solution with the electronic components to wet the electronic components. One skilled in the art will recognize that these methods of wetting the electronic components can be varied to adjust the thickness of the layer of wetting solution on the electronic components. For example, in the case of where the electronic components are immersed in a wetting solution, the slower the withdrawal of wetting solution from the electronic components, the thinner the layer will be on the electronic components.



The temperature of the wetting solution during contact with the electronic components is preferably from about room temperature to about the condensation temperature of the wetting solution. The temperature of the wetting solution may be for example from about 25 °C to about 100 °C, more preferably from about 30 °C to about 80 °C, and most preferably  
5 from about 35 °C to about 60 °C. The pressure of the wetting solution during contact with the electronic components is preferably from about 0 psig to about 20 psig.

The electronic components in the methods of the present invention are also contacted with an ozonated process fluid. The ozonated process fluid may be any fluid that contains gaseous ozone and is in the form of a gas, vapor, mist or combinations thereof. The ozonated  
10 process fluid may be for example gaseous ozone, or a combination of gaseous ozone and one or more other process fluids. Preferably, the other process fluids present in the ozonated process fluid are in the form of a vapor, gas, mist or combinations thereof. By having the one or more other process fluids in a gas, vapor, or mist, the stability of the gaseous ozone is increased in comparison to ozone dissolved in a liquid, thereby increasing the chances that the  
15 gaseous ozone will reach the surfaces of the electronic components for reaction (such as with organic materials located on the surfaces of the electronic components).

Preferably, the concentration of ozone in the ozonated process fluid expressed as weight of ozone per volume of ozonated process fluid is from about 10 g/m<sup>3</sup> to about 300 g/m<sup>3</sup>, more preferably from about 50 g/m<sup>3</sup> to about 250 g/m<sup>3</sup>, and most preferably from about  
20 100 g/m<sup>3</sup> to about 200 g/m<sup>3</sup> at standard temperature and pressure (25 °C, 1 atm). Although the temperature of the ozonated process fluid that is contacted with the electronic components will depend upon the ozonated process fluid chosen, in general, the temperature of the ozonated process fluid preferably ranges from about 20 °C to about 145 °C and more preferably from about 40 °C to about 120 °C. The pressure of the ozonated process fluid during contact with  
25 the electronic components is preferably from about 0 psig to about 20 psig, more preferably from about 1 psig to about 10 psig, and most preferably from about 1 psig to about 5 psig.

As mentioned previously, the ozonated process fluid may also contain other process fluids in addition to gaseous ozone. For example, in a preferred embodiment of the present invention, the ozonated process fluid contains a hydroxide fluid. By "hydroxide fluid," it is  
30 meant any process fluid, in the form of a gas, vapor, mist, or combinations thereof, that promotes the formation of hydroxyl radicals alone or in combination with other reactants in the presence of ozone. For example, the hydroxide fluid may contain compounds having

hydroxyl functional groups that promote the formation of hydroxyl radicals, or the hydroxide fluid may be a base, or combinations thereof.

Suitable hydroxide fluids include for example water; hydrogen peroxide; or bases that are capable of providing, alone or in combination with another process fluid such as water, hydroxide ions; or any combination thereof. Bases useful in the present invention include inorganic bases and organic bases. Suitable bases include for example, ammonia, ammonium hydroxide, alkyl ammonium hydroxides, such as trimethyl ammonium hydroxide, alkali or alkaline earth metal hydroxides such as sodium hydroxide or potassium hydroxide; organic amines; basic amino acids; or combinations thereof. Preferred bases include ammonia, ammonium hydroxide, trimethylammonium hydroxide, organic amines, or combinations thereof. The most preferred hydroxide fluids useful in the methods of the present invention are water, ammonia, ammonium hydroxide, trimethylammonium hydroxide or combinations thereof.

The concentration of the hydroxide fluid in the ozonated process fluid will depend upon such process parameters as the type of hydroxide fluid being used. For example in the case of a base, preferably the base will be added in an amount to provide a pH of from about 9 to about 13 at the surfaces of the electronic components, taking into account the water present from the wetting solution and any hydroxide fluids from the ozonated process fluid deposited on the electronic components. In the case water and hydrogen peroxide, preferably the molar ratio of ozone to hydroxide fluid is from about 1:90 to about 40:1, more preferably from about 1:10 to about 20:1, and most preferably from about 1:2 to about 2:1.

In addition to the hydroxide fluid, other process fluids may be present in the ozonated process fluid. Examples of other process fluids include for example alcohols, such as  $C_1$  to  $C_{20}$  alcohols, and more preferably  $C_1$  to  $C_6$  alcohols such as methanol, ethanol, propanol (e.g., isopropanol), butanol, pentanol, or hexanol; hydrogen chloride; hydrogen fluoride; carbon dioxide; or combinations thereof. As acetic acid is a hydroxyl radical scavenger, preferably, the reaction chamber is substantially free of acetic acid when gaseous ozone is present in the reaction chamber to prevent the scavenging of hydroxyl radicals. The other process fluids may be present in the ozonated process fluid to preferably provide a molar ratio of ozone to the other process fluids in the ozonated process fluid in an amount of from about 1:90 to about 40:1.

The preferred temperatures of the process fluids prior to formation of the ozonated process fluid (e.g., hydroxide fluid or other process fluids) will depend on the form of the process fluid. For example, where the process fluid is a gas such as ammonia, preferably the process fluid is not heated prior to formation of the ozonated process fluid. Where the process fluid is a mist, preferably the temperature of the process fluid ranges from about room temperature to the condensation temperature of the process fluid. In the case of water, this temperature is preferably from about 20 °C to about 100 °C. Where the process fluid is a vapor, preferably the vapor is at a temperature above its condensation temperature, and more preferably at a temperature to permit condensation of the vapor on the surfaces of the electronic components. In this regard, it may be desirable to have the electronic components at a temperature at, or slightly below the vapor condensation temperature (e.g., more than 20° C below) to enhance condensation.

There are various ways in which the ozonated process fluid may be formed. Preferably the method of formation does not significantly promote the degradation of ozone. For example, the ozonated process fluid may be formed by adding each process fluid separately into a reaction chamber containing wetted electronic components prior to or during the addition of the gaseous ozone. The ozonated process fluid may also be formed by combining ozone and/or any of the process fluids together prior to addition to the reaction chamber containing the electronic components. Where it is desired to combine ozone with any process fluids prior to addition to the reaction chamber, the process fluids are preferably in a form to minimize their reaction with ozone. For example, if it is desired to combine gaseous ozone and a base prior to entering the reaction chamber, preferably, the base is a gas such as ammonia, as the reaction of ozone in a gas is slower in comparison to the reaction of ozone in a mist or vapor. To avoid the risk of degrading the ozone, preferably the ozone is added to the reaction chamber separately from the other process fluids to form the ozonated process fluid.

The sequence of addition of the components of the ozonated process fluid can also be staggered to enhance the formation of hydroxyl radicals at the surfaces of the electronic components. For example, in a preferred embodiment of the present invention, the process fluids in the ozonated process fluid are added slightly before and optionally during the addition of the gaseous ozone. By following this sequence, the electronic components can be coated with a thin layer of one or more process fluids (such as water and/or base) to facilitate the

reaction of the ozone in this layer to form hydroxyl radicals. Another advantage to this method is that the gaseous ozone is not given the opportunity to react with the process fluids in the ozonated process fluid until reaching the surfaces of the electronic components.

Some specific embodiments of forming the ozonated process fluid in accordance with the methods of the present invention will now be described. These embodiments are being provided as examples only and are in no way intended to limit the scope of the present invention.

In one embodiment of the present invention gaseous ozone and a vapor of water may be combined under pressure to form the ozonated process fluid. This ozonated process fluid can then be expanded when introduced into the reaction chamber by using, for example, a throttle valve.

In another embodiment of the present invention gaseous ozone and a hydroxide fluid may be added to a reaction chamber containing electronic components from separate openings, and combined in the reaction chamber to form an ozonated process fluid. When added separately, the gaseous ozone and hydroxide fluid may be supplied for example from opposing openings to enhance formation of hydroxyl radicals at the surfaces of the electronic components.

In another embodiment of the present invention, the gaseous ozone and hydroxide fluid may be combined by spraying the hydroxide fluid in the form of a mist into the reaction chamber prior to and/or during the addition of gaseous ozone to the reaction chamber so that the ozone is combined with the mist in the reaction chamber. The mist can be created by any technique known to those skilled in the art such as through the use of ultrasonic or megasonic mistifiers, jets, atomizers, or spray nozzles. In a preferred embodiment, the gaseous ozone is added at the bottom of the reaction chamber and the hydroxide fluid is added from the top of the reaction chamber. The mist may be for example a deionized water mist or a mist of a base dissolved in water.

Preferably, the mist is supplied to the reaction chamber at a temperature below the condensation temperature of the hydroxide fluid. For example, for a deionized water mist or mist of base dissolved in water, preferably the temperature is from about 25°C to about 90 °C, and more preferably from about 30°C to about 50° C. The ozone is preferably supplied to the reaction chamber at a temperature of from about 25°C to about 50 °C and a pressure of from about 1 psig to about 20 psig. An advantage to using an ozonated process fluid containing a



mixture of a mist of hydroxide fluid and gaseous ozone is that the gaseous ozone has a longer lifetime in a mist in comparison to ozone dissolved in bulk liquid, and even in comparison to ozone mixed with a vapor having an elevated temperature (e.g., greater than 90 °C).

In another embodiment of the present invention the ozonated process fluid may be formed from ozonated water. Ozonated water is formed by dissolving gaseous ozone in a solution containing water according to techniques well known to those skilled in the art. For example, the dissolving of ozone is performed at a temperature and pressure to enhance the solubility of the ozone in the water. The ozonated water is then treated, for example through evaporation of the ozonated water to form an ozonated process fluid containing ozone and water vapor.

After the ozone has been dissolved, there are various ways in which the ozonated water may be treated to form the ozonated process fluid. For example, in one embodiment, the ozonated process liquid may be evaporated using heat to form an ozonated process fluid containing ozone and water vapor.

In another embodiment, ozonated water is contacted with a carrier gas, such as nitrogen. The carrier gas preferably "picks-up" or evaporates the gaseous ozone and water vapor to form an ozonated process fluid containing the carrier gas, ozone, and water vapor. The contacting of the carrier gas with the ozonated process liquid may be carried out by any technique known to those skilled in the art such as through sparging or bubbling the carrier gas through the ozonated process liquid. The carrier gas during contact with the ozonated water is preferably at a temperature below the boiling point of the ozonated water.

The ozonated process fluid once formed, is preferably, immediately contacted with the electronic components in a reaction chamber for a time to accomplish the desired result. The temperature of the electronic components during contacting is preferably at or slightly below the temperature of the ozonated process fluid. By "contact time," as used herein, it is meant the time an electronic component is exposed to a process fluid. For example, the contact time will include the time an electronic component is exposed to the process fluid during filling a vessel with the process fluid or immersing the electronic component in the process fluid; the time the electronic component is soaked in the process fluid; and the time the electronic component is exposed to the process fluid while the process fluid or electronic component is being removed from the vessel. The actual contact time chosen will also depend on such variables as the temperature, pressure, and composition of the ozonated process fluid, and the



composition of the surfaces of the electronic components. Preferably, the contact time with the ozonated process fluid will be for at least 30 seconds.

Preferably, the contacting of the ozonated process fluid is performed subsequent to wetting the electronic components with the wetting solution to ensure that there is a layer of wetting solution on the electronic components. However, it is possible to simultaneously contact the electronic components with the wetting solution for at least a portion of the time that the electronic components are contacted with the ozonated process fluid as long as the electronic components are wetted by the wetting solution prior to ceasing the flow of ozone to the reaction chamber.

As mentioned previously, the ozonated process fluid is contacted with the electronic components in the presence of at least one base that is present in the ozonated process fluid (e.g., as a hydroxide fluid previously described herein), or is present in the wetting solution, or is present in both the ozonated process fluid and wetting solution. If it is desired to include a base in the ozonated process fluid, preferably the base is combined with the gaseous ozone according to the methods previously described to minimize the base degrading the ozone prior to reaching the surfaces of the electronic components.

There various ways in which the electronic components can be contacted with the ozonated process fluid in the presence of a base for at least a portion of the contact time with the ozonated process fluid. Some specific embodiments of contacting the ozonated process fluid with the electronic components in the presence of a base will now be described. These embodiments are being provided as examples only and are in no way intended to limit the scope of the present invention.

In one embodiment of the present invention, the electronic components are contacted with a wetting solution of water and then contacted with an ozonated process fluid containing gaseous ozone, water vapor, and a base. In this embodiment, the base is preferably a gas, vapor or combination thereof and is selected from ammonia, an alkyl ammonium hydroxide, an organic amine, or combinations thereof, and is most preferably selected from ammonia. The ozonated process fluid is preferably formed by separately adding ozone, water vapor, and ammonia to the reaction chamber. The deionized water vapor is preferably supplied at a pressure of from about 1 psig to about 20 psig and temperature of from about 70 °C to about 140 °C. The ozone and ammonia is preferably supplied at pressures ranging from about 1 psig to about 20 psig and temperatures of from about 25 °C to about 50 °C.

In another embodiment of the present invention, the electronic components are contacted with a wetting solution of water and then contacted with an ozonated process fluid containing ozone and a base dissolved in an aqueous solution (e.g., the base is an aqueous solution of ammonium hydroxide, or an alkali or an alkaline earth metal hydroxide). In this  
5 embodiment, the base is preferably added to the reaction chamber as a mist in a separate stream from the ozone.

In a preferred embodiment of the invention, the electronic components are contacted with a wetting solution containing a base (hereinafter "basic solution") and contacted with an ozonated process fluid. Preferably, the basic solution contains ammonium hydroxide or an  
10 alkali or alkaline metal hydroxide solution. The ozonated process fluid may be for example pure gaseous ozone, or a mixture of a hydroxide fluid (e.g., water and/or base) and ozone.

In this embodiment, there are various ways in which the basic solution and ozonated process fluid could be fed to the reaction chamber. For example, the basic solution could be fed to the reaction chamber in the form of a mist prior to or during the addition of the ozonated  
15 process fluid to the reaction chamber. The basic solution could also be applied to the electronic components by filling the reaction chamber containing the electronic components with the basic solution. In this embodiment, the ozonated process fluid may be added to the reaction chamber during (such as through direct displacement of the basic solution with the ozonated process fluid) or after removal of the basic solution from the reaction chamber.

20 In another preferred embodiment of the present invention, the electronic components are contacted with a wetting solution that is a mist of water and contacted with an ozonated process fluid containing ammonia and gaseous ozone during and/or after contacting the electronic components with the wetting solution. The gaseous ozone and ammonia are preferably added separately to the reaction chamber in this embodiment.

25 In addition to the ozonated process fluid, the electronic components may be contacted with any number of other reactive chemical process fluids (e.g., gas, liquid, vapor or any combination thereof) to achieve the desired result. For example, the electronic components may be contacted with reactive chemical process fluids used to etch (hereinafter referred to as etching fluids), grow an oxide layer (hereinafter referred to as oxide growing fluids), to  
30 remove photoresist (hereinafter referred to as photoresist removal fluids), to enhance cleaning (hereinafter referred to as cleaning fluids), or combinations thereof. The electronic

components may also be rinsed with a rinsing fluid at any time during the wet processing method. Preferably, the reactive chemical process fluids and rinsing fluids are liquids.

The reactive chemical process fluids useful in the present invention contain one or more chemically reactive agents to achieve the desired surface treatment. Preferably, the concentration of such chemically reactive agents will be greater than 1000 ppm and more preferably greater than 10,000 ppm, based on the weight of the reactive chemical process fluid. However, in the case of ozone, generally the concentration is equal to or greater than about 10 ppm and more preferably from about 10 ppm to about 50 ppm. Examples of chemically reactive agents include for example hydrochloric acid or buffers containing the same, ammonium hydroxide or buffers containing the same, hydrogen peroxide, sulfuric acid or buffers containing the same, mixtures of sulfuric acid and ozone, hydrofluoric acid or buffers containing the same, chromic acid or buffers containing the same, phosphoric acid or buffers containing the same, acetic acid or buffers containing the same, nitric acid or buffers containing the same, ammonium fluoride buffered hydrofluoric acid, deionized water and ozone, or combinations thereof.

It is also possible for the reactive chemical process fluid to contain 100% of one or more chemically reactive agents. For example, it may be desired to contact the electronic components with solvents such as acetone, N-methyl pyrrolidone, or combinations thereof. Such solvents are chemically reactive agents used, for example, to remove organics or to provide other cleaning benefits.

Examples of preferred reactive chemical process fluids useful in the present invention include cleaning fluids, etching fluids, and photoresist removal fluids. Cleaning fluids typically contain one or more corrosive agent such as an acid or base. Suitable acids for cleaning include for example sulfuric acid, hydrochloric acid, nitric acid, or aqua regia. Suitable bases include for example, ammonium hydroxide. The desired concentration of the corrosive agent in the cleaning fluid will depend upon the particular corrosive agent chosen and the desired amount of cleaning. These corrosive agents may also be used with oxidizing agents such as ozone or hydrogen peroxide. Preferred cleaning solutions are "SC1" solutions containing water, ammonia, and hydrogen peroxide, and "SC2" solutions containing water, hydrogen peroxide, and hydrochloric acid. Typical concentrations for SC1 solutions range from about 5:1:1 to about 200:1:1 parts by volume  $H_2O$  :  $H_2O_2$  :  $NH_4OH$ . Typical concentrations for SC2 solutions range from about 5:1:1 to about 1000:0:1 parts by volume

H<sub>2</sub>O : H<sub>2</sub>O<sub>2</sub>:HCl. Suitable etching solutions contain agents that are capable of removing oxides. A common etching agent used is for example hydrofluoric acid, buffered hydrofluoric acid, ammonium fluoride, or other substances which generate hydrofluoric acid in solution. A hydrofluoric acid containing etching solution may contain for example from about 4:1 to  
5 about 1000:1 parts by weight H<sub>2</sub>O :HF.

One skilled in the art will recognize that there are various process fluids that can be used during wet processing. Other examples of process fluids that can be used during wet processing are disclosed in "Chemical Etching" by Werner Kern et al., in *Thin Film Processes*, edited by John L. Vossen et al., published by Academic Press, NY 1978, pages 401-496, which  
10 is incorporated by reference in its entirety.

The electronic components may also be contacted with rinsing fluids during the methods of the present invention. As previously described, rinsing fluids are used to remove from the electronic components and/or vessel residual reactive chemical process fluids, reaction by-products, and/or particles or other contaminants freed or loosened by a chemical  
15 treatment step. The rinsing fluids may also be used to prevent redeposition of loosened particles or contaminants onto the electronic components or vessel.

Any rinsing fluid may be chosen that is capable of achieving the effects described above. In selecting a rinsing fluid, such factors as the nature of the surfaces of the electronic components to be rinsed, the nature of contaminants dissolved in the reactive chemical process  
20 fluid, and the nature of the reactive chemical process fluid to be rinsed should be considered. Also, the proposed rinsing fluid should be compatible (i.e., relatively nonreactive) with the materials of construction in contact with the fluid. Rinsing fluids which may be used include for example water, organic solvents, mixtures of organic solvents, ozonated water, or combinations thereof. Preferred organic solvents include those organic compounds useful as  
25 drying solutions disclosed hereinafter such as C<sub>1</sub> to C<sub>10</sub> alcohols, and preferably C<sub>1</sub> to C<sub>6</sub> alcohols. Preferably the rinsing fluid is a liquid and more preferably is deionized water.

Rinsing fluids may also optionally contain low levels of chemically reactive agents to enhance rinsing. For example, the rinsing fluid may be a dilute aqueous solution of hydrochloric acid or acetic acid to prevent, for example, metallic deposition on the surface of  
30 the electronic component. Surfactants, anti-corrosion agents, and/or ozone are other additives used in rinsing fluids. The concentration of such additives in the rinsing fluid is minute. For example, the concentration is preferably not greater than about 1000 ppm by weight and more



preferably not greater than 100 ppm by weight based on the total weight of the rinsing fluid. In the case of ozone, preferably the concentration of ozone in the rinsing fluid is 5 ppm or less.

One skilled in the art will recognize that the selection of reactive chemical process fluids, the sequence of reactive chemical process fluids and rinsing fluids, and the processing conditions (e.g., temperature, concentration, contact time and flow of the process fluid) will depend upon the desired wet processing results. For example, the electronic components could be contacted with a rinsing fluid before or after one or more chemical treatment steps. Alternatively, it may be desired in some wet processing methods to have one chemical treatment step directly follow another chemical treatment step, without contacting the electronic components with a rinsing fluid between two chemical treatment steps (i.e., no intervening rinse). Such sequential wet processing, with no intervening rinse, is described in for example U.S. application Serial No. 08/684,543 filed July 19, 1996, which is hereby incorporated by reference in its entirety.

In a preferred embodiment of the present invention, the electronic components are contacted with at least one processing fluid that is a liquid (i.e., processing solution) subsequent to contact with the ozonated process fluid to aid in removal of reaction by products or residual chemicals such as oxidized organic material. This subsequent contacting of the electronic components is especially preferred when the ozonated process fluid is used to remove organic materials from the surfaces of the electronic components. The processing solution may be a reactive chemical process liquid or rinsing liquid or combinations thereof.

For example, in one embodiment of the present invention, the electronic components after contact with an ozonated process fluid, are contacted with a cleaning solution such as an SC1 solution and/or an SC2 solution. Following contact with the SC1 and/or SC2 solution, the electronic components may be optionally rinsed with a rinsing liquid such as deionized water. Preferably, the SC1 Solution is at a temperature of from about 15°C to about 95°C, and more preferably from about 25°C to about 45°C. Preferably, the SC2 Solution is at a temperature of from about 15°C to about 95°C, and more preferably from about 25°C to about 45°C. Preferably, the rinsing liquid is at a temperature of from about 15°C to about 90°C, and more preferably from about 25°C to about 30°C.

In another embodiment of the present invention, the electronic components may be contacted with an etching solution subsequent to contact with the ozonated process fluid.



Where the etching solution contains hydrofluoric acid, preferably the temperature of the hydrofluoric acid is from about 15 °C to about 95 °C, and more preferably from about 35 °C to about 40 °C. Following etching, the electronic components may be contacted with a rinsing liquid such as deionized water. Preferably the temperature of the rinsing liquid is from about 5 15 °C to 90 °C, and more preferably from about 25 °C to about 30 °C.

In another embodiment of the present invention, the electronic components, after contact with an ozonated process fluid, may be contacted with an SC1 solution having a concentration of about 80:3:1 parts by volume H<sub>2</sub>O: H<sub>2</sub>O<sub>2</sub>: NH<sub>4</sub>OH; an SC2 solution having a concentration of 80:1:1 parts by volume H<sub>2</sub>O:H<sub>2</sub>O<sub>2</sub>:HCl; and a hydrofluoric acid solution 10 having a concentration of about 4:1 to about 1000:1 parts by volume H<sub>2</sub>O:HF. This method is particularly useful for cleaning and etching. The order of treatment of the SC1 solution, the SC2 solution, and the etching solution may also be reversed.

In a preferred embodiment of the present invention the electronic components, after contact with the ozonated process fluid, are contacted with an SC1 solution, and then 15 contacted with an SC2 solution. The electronic components are then preferably rinsed with deionized water and dried using an isopropanol vapor.

Thus, there are various types of ways in which the electronic components can be wet processed in accordance with the method of the present invention. For example, wet processing can be carried out using sonic energy (such as in the megasonic energy range) 20 during the contacting of the electronic components with a process liquid to enhance cleaning. Such methods may also include wet processing techniques disclosed in for example U.S. Patent No. 5,383,484; U.S. Patent Application Ser. Nos. 08/684,543, filed July 19, 1996; 09/209,101, filed December 10, 1998; and 09/253,157, filed February 19, 1999; and U.S. Provisional Patent Application Ser. Nos. 60/087,758 filed June 2, 1998; and 60/111,350 filed 25 December 8, 1998, the disclosures of which are all hereby incorporated by reference in their entireties.

The methods of the invention may be carried out in generally any wet processing equipment including for example multiple bath systems (e.g., wet bench), and single vessel systems (open or closable to the environment). *See, e.g.*, Chapter 1: Overview and Evolution 30 of Semiconductor Wafer Contamination and Cleaning Technology by Werner Kern and Chapter 3: Aqueous Cleaning Processes by Don C. Burkman, Donald Deal, Donald C. Grant, and Charlie A. Peterson in Handbook of Semiconductor Wafer Cleaning Technology (edited

by Werner Kern, Published by Noyes Publication Parkridge, New Jersey 1993), and Wet Etch Cleaning by Hiroyuki Horiki and Takao Nakazawa in Ultraclean Technology Handbook, Volume 1, (edited by Tadahiro Ohmi published by Marcel Dekker), the disclosures of which are herein incorporated by reference in their entirety.

5 Preferably the wet processing system will also include storage tanks for chemical reagents, such as ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) or hydrofluoric acid ( $\text{HF}$ ); and a system for delivering deionized water used for rinsing the electronic components and diluting the chemical reagents. The chemical reagents are preferably stored in their concentrated form, which is: hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) (31%),  $\text{NH}_4\text{OH}$  (28%), hydrochloric acid ( $\text{HCl}$ ) (37%),  
10  $\text{HF}$  (49%), and sulfuric acid ( $\text{H}_2\text{SO}_4$ ) (98%) (percentages represent weight percentages in aqueous solutions). The storage tanks are preferably set-up so that they are in fluid communication with the reaction chamber where the electronic components are treated.

The gaseous ozone is preferably produced externally to the wet processing reaction chamber. Ozone may be generated by any method known to those skilled in the art without  
15 departing from the spirit of the invention. Preferably, ozone is generated with a high capacity generator such as a TEX8200 capable of producing roughly 100 grams/hr or greater.

In a preferred embodiment of the invention, the electronic components are housed in a single vessel system. Preferably, single vessel systems such as those disclosed in U.S. Patent Nos. 4,778,532, 4,917,123, 4,911,761, 4,795,497, 4,899,767, 4,984,597, 4,633,893, 4,917,123,  
20 4,738,272, 4,577,650, 5,571,337 and 5,569,330, the disclosures of which are herein incorporated by reference in their entirety, are used. Preferred commercially available single vessel systems are Full-Flow™ vessels such as those manufactured by CFM Technologies, Poseidon manufactured by Steag, and FL820L manufactured by Dainippon Screen. Such systems are preferred because foreign gas and contamination levels can be more readily  
25 controlled.

The single vessel wet processing system also preferably includes metering devices such as a control valve and/or pump for transporting chemical reagents from the storage tank area to the reaction chamber. A processing control system, such as a personal computer, is also typically used as a means to monitor processing conditions (*e.g.*, flow rates, mix rates,  
30 exposure times, and temperature). For example, the processing control system can be used to program the flow rates of chemical reagents and deionized water so that the appropriate concentration of chemical reagent(s) will be present in the reactive chemical process fluid.

In a most preferred embodiment of the present invention, the electronic components are wet processed in an enclosable single vessel wet processing system. The enclosable single vessel wet processing system is also preferably capable of receiving different process fluids in various sequences. A preferred method of delivering process fluids to the vessel is by direct displacement of one fluid with another. The Full Flow™ wet processing system manufactured by CFM Technologies, Inc is an example of a system capable of delivering fluids by direct displacement. Such systems are preferred because they result in a more uniform treatment of the electronic components. Additionally, often the chemicals utilized in the chemical treatment of electronic components are quite dangerous in that they may be strong acids, alkalis, or volatile solvents. Enclosable single vessels minimize the hazards associated with such process fluids by avoiding atmospheric contamination and personnel exposure to the chemicals, and by making handling of the chemicals safer.

In a preferred method of the present invention using a single, enclosable vessel, one or more electronic components are placed in a single vessel and closed to the environment. The electronic components may optionally be contacted with one or more process fluids for pretreatment. Following any desired pretreatment step, the electronic components are contacted with a wetting solution, such as a basic solution, to wet the surfaces of the electronic components. Such contacting can be accomplished through directing the wetting solution into the vessel to fill the process vessel full with the wetting solution so that gases from the atmosphere or residual fluid from a previous step are not significantly trapped within the vessel. The fluid can be continuously directed through the vessel once the vessel is full of the wetting solution, or the flow of wetting solution can be stopped to soak the electronic components for a desired time. The wetting solution may then be removed from the vessel and the ozonated process fluid may be directed into the vessel to contact the electronic components with the ozonated process fluid. A base is preferably present in the vessel for at least a portion of the time that the electronic components are contacted with the ozonated process fluid. Following contact with the ozonated process fluid, the electronic components may be optionally rinsed with a rinsing fluid and/or contacted with another process fluid such as one or more reactive chemical process fluids.

The removal of one process fluid with another process fluid in the enclosable single vessel can be accomplished in several ways. For example, the process fluid in the process vessel can be completely removed (i.e., drained), and then the next process fluid can be

directed into the vessel during or after draining. In another embodiment, the process fluid present in the vessel can be directly displaced by the next desired process fluid as described for example in U.S. Patent No. 4,778,532.

Following wet processing with reactive chemical process fluids or rinsing fluids, the electronic components are preferably dried. By "dry" or "drying" it is meant that the electronic components are preferably made substantially free of liquid droplets. By removing liquid droplets during drying, impurities present in the liquid droplets do not remain on the surfaces of the semiconductor substrates when the liquid droplets evaporate. Such impurities undesirably leave marks (e.g., watermarks) or other residues on the surfaces of the semiconductor substrates. However, it is also contemplated that drying may simply involve removing a treating, or rinsing fluid, for example with the aid of a drying fluid stream, or by other means known to those skilled in the art.

Any method or system of drying may be used. Suitable methods of drying include for example evaporation, centrifugal force in a spin-rinser-dryer, steam or chemical drying, or combinations thereof. In a preferred embodiment, the wet processing and drying is performed in a single vessel without removing the electronic components from the vessel.

A preferred method of drying uses a drying fluid stream to directly displace the last processing solution that the electronic components are contacted with prior to drying (hereinafter referred to as "direct displace drying"). Suitable methods and systems for direct displace drying are disclosed in for example U.S. Patent Nos. 4,778,532, 4,795,497, 4,911,761, 4,984,597, 5,571,337, and 5,569,330. Other direct displace dryers that can be used include Marangoni type dryers supplied by manufacturers such as Steag, Dainippon, and YieldUp.

Preferably, the drying fluid stream is formed from a partially or completely vaporized drying solution. The drying fluid stream may be for example superheated, a mixture of vapor and liquid, saturated vapor or a mixture of vapor and a noncondensable gas.

The drying solution chosen to form the drying fluid stream is preferably miscible with the last process fluid in the vessel and non-reactive with the surfaces of the electronic components. The drying solution also preferably has a relatively low boiling point to facilitate drying. For example, the drying solution is preferably selected from organic compounds having a boiling point of less than about 140 degrees centigrade at atmospheric pressure. Examples of drying solutions which may be employed are steam, alcohols such as methanol, ethanol, 1-propanol, isopropanol, n-butanol, secbutanol, tertbutanol, or tert-amyl alcohol,



acetone, acetonitrile, hexafluoroacetone, nitromethane, acetic acid, propionic acid, ethylene glycol mono-methyl ether, difluoroethane, ethyl acetate, isopropyl acetate, 1,1,2-trichloro-1,2,2-trifluoroethane, 1,2-dichloroethane, trichloroethane, perfluoro-2-butyltetrahydrofuran, perfluoro-1,4-dimethylcyclohexane or combinations thereof.

- 5 Preferably, the drying solution is a C<sub>1</sub> to C<sub>6</sub> alcohol, such as for example methanol, ethanol, 1-propanol, isopropanol, n-butanol, secbutanol, tertbutanol, tert-amyl alcohol, pentanol, hexanol or combinations thereof.

In a preferred embodiment of the present invention a drying solution is selected which is miscible with the processing solution present in the process vessel immediately before  
10 drying and forms a minimum-boiling azeotrope with the processing solution. Since water is the most convenient and commonly used solvent for chemical treatment or rinsing fluids, a drying solution which forms a minimum-boiling azeotrope with water is especially preferred.

Following drying, the electronic components may be removed from the drying vessel and further processed in any desired manner.

- 15 Although the present invention has been described above with respect to particular preferred embodiments, it will be apparent to those skilled in the art that numerous modifications and variations can be made to those designs. The descriptions provided are for illustrative purposes and are not intended to limit the invention.



What is claimed is:

1. A method of wet processing electronic components comprising:
  - (a) contacting the surfaces of the electronic components with a wetting solution to wet the surfaces of the electronic components with the wetting solution, wherein the wetting  
5 solution comprises water;
  - (b) forming an ozonated process fluid comprising gaseous ozone, wherein the ozonated process fluid is in the form of a gas, vapor, mist, or mixtures thereof; and
  - (c) contacting the electronic components with the ozonated process fluid in a reaction chamber for a contact time and in the presence of at least one base for at least a  
10 portion of the contact time, wherein the ozonated process fluid is at a temperature of from about 20 °C to about 145 °C, and the base is present in the wetting solution or the ozonated process fluid, or combinations thereof.
2. The method of Claim 1 further comprising the step of contacting the electronic components with at least one processing solution after the contacting of the electronic  
15 components with the ozonated process fluid.
3. The method of Claim 1 wherein the base is selected from the group consisting of ammonia, ammonium hydroxide, an alkyl ammonium hydroxide, an alkali metal hydroxide, an alkaline earth metal hydroxide, an organic amine, a basic amino acid, and combinations thereof.
- 20 4. The method of Claim 3 wherein the base is present in the wetting solution.
5. The method of Claim 4 wherein the base is selected from the group consisting of ammonium hydroxide, an alkyl ammonium hydroxide, an alkali metal hydroxide, an alkaline earth metal hydroxide and combinations thereof.
6. The method of Claim 3 wherein the base is present in the ozonated process  
25 fluid, is in the form of a vapor, gas, or combinations thereof, and is selected from the group consisting of ammonia, an alkyl ammonium hydroxide, an organic amine and combinations thereof.

7. The method of Claim 1 wherein the ozonated process fluid further comprises a hydroxide fluid comprising water, hydrogen peroxide, a base, or combinations thereof.

8. The method of Claim 7 wherein the ozonated process fluid is formed by combining the gaseous ozone and the hydroxide fluid in the reaction chamber.

5 9. The method of Claim 8 wherein the hydroxide fluid is ammonia, a mist of water, water vapor or combinations thereof.

10 10. The method of Claim 1 wherein the ozonated process fluid is formed by combining ozone and water to form ozonated water, and bubbling a carrier gas in the ozonated water to form the ozonated process fluid comprising water vapor, the ozone, and the carrier gas.

11. A method of wet processing electronic components comprising:  
(a) loading in an enclosable single vessel a plurality of electronic components;  
(b) contacting the surfaces of the electronic components with a wetting solution to wet the surfaces of the electronic components with the wetting solution, wherein the  
15 wetting solution comprises water;

(c) forming an ozonated process fluid comprising gaseous ozone wherein the ozonated process fluid is in the form of a gas, vapor, mist, or mixtures thereof;

(d) contacting the electronic components with the ozonated process fluid in a reaction chamber for a contact time and in the presence of at least one base for at least a  
20 portion of the contact time, wherein the ozonated process fluid is at a temperature of from about 20 °C to about 145 °C, and the base is present in the wetting solution or the ozonated process fluid, or combinations thereof; and

(e) contacting the electronic components in the vessel with one or more processing solutions after the contacting of the electronic components with the ozonated process fluid.

12. The method of Claim 11 wherein the base is selected from the group consisting of ammonia, ammonium hydroxide, an alkyl ammonium hydroxide, an alkali metal hydroxide, an alkaline earth metal hydroxide, an organic amine, a basic amino acid, and combinations thereof.
- 5 13. The method of Claim 12 wherein the base is present in the wetting solution.
14. The method of Claim 13 wherein the base is selected from the group consisting of ammonium hydroxide, an alkyl ammonium hydroxide, an alkali metal hydroxide, an alkaline earth metal hydroxide and combinations thereof.
- 10 15. The method of Claim 12 wherein the base is present in the ozonated process fluid, is in the form of a vapor, gas, or combinations thereof, and is selected from the group consisting of ammonia, an alkyl ammonium hydroxide, an organic amine and combinations thereof.
16. The method of Claim 11 wherein the ozonated process fluid further comprises a hydroxide fluid comprising water, hydrogen peroxide, a base, or combinations thereof.
- 15 17. The method of Claim 16 wherein the ozonated process fluid is formed by combining the gaseous ozone and the hydroxide fluid in the vessel.
18. The method of Claim 17 wherein the hydroxide fluid is ammonia, a mist of water, water vapor or combinations thereof.
19. The method of Claim 18 wherein the hydroxide fluid is ammonia.
- 20 20. The method of Claim 11 wherein the electronic components are contacted with the wetting solution by filling the vessel with the wetting solution, and wherein the electronic components are contacted with the ozonated process fluid by directing the ozonated process fluid into the vessel during or after removal of the wetting solution from the vessel.

21. The method of Claim 11 wherein the at least one of the processing solutions comprises water, hydrogen peroxide and ammonium hydroxide.

22. The method of Claim 21 wherein the electronic components are dried in the vessel.

5 23. A method of wet processing electronic components comprising:

(a) contacting electronic components with a wetting solution to wet the surfaces of the electronic components with the wetting solution, wherein the wetting solution comprises water and at least one base;

(b) contacting the wetted electronic components with an ozonated process fluid for  
10 a contact time, wherein the ozonated process fluid is in the form of a gas, vapor, mist, or mixtures thereof, and wherein the ozonated process fluid is at a temperature of from about 20 ° C to about 145 ° C; and

(c) contacting the electronic components with one or more processing fluids after the contacting of the electronic components with the gaseous ozone.

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24. The method of Claim 23 wherein the ozonated process fluid is gaseous ozone, or a mixture comprising gaseous ozone and at least one hydroxide fluid.

25. The method of Claim 23 wherein the base in the wetting solution is selected from the group consisting of ammonium hydroxide, an alkyl ammonium hydroxide, an alkali  
20 metal hydroxide, an alkaline earth metal hydroxide, an organic amine, a basic amino acid and combinations thereof.

26. The method of Claim 25 wherein the ozonated process fluid further comprises a second base.

27. The method of Claim 26 wherein the second base is ammonia.

28. The method of Claim 23 wherein the electronic components are contacted with the wetting solution by filling the vessel with the wetting solution, and wherein the electronic components are contacted with the ozonated process fluid by directing the ozonated process fluid into the vessel during or after removal of the wetting solution from the vessel.